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Tracing the source of ancient reworked organic matter delivered to the North Atlantic Ocean during Heinrich Events

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Abstract

A major effort of the geochemical and paleoclimate community has been to identify the specific sources of the ice-rafted debris (IRD) in Heinrich Layers (HLs). Although the general consensus is that the majority of the IRD originated from the Hudson area of northern Canada, the specific sources are not well constrained. Here we compare the diagnostic organic geochemical signature of HLs to that of a number of Paleozoic outcrops across the former margin of the Laurentide ice sheet.

We show that the biomarker signature of Upper Ordovician strata from Southampton and Baffin Island is compatible with that found in HLs in the Labrador Sea and North Atlantic, while the biomarker signature of other Paleozoic formations from the former margin of the Laurentide ice sheet is not. In addition to the biomarker signature, key-inorganic characteristics ($\delta^{18}\text{O}$, ϵ_{Nd} , and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios) of these formations from Southampton and Baffin Island are consistent with those reported from HLs. The location of these formations in and around the Hudson Strait is compatible with palaeo-ice flow regimes through the Hudson Strait,

allowing for easy entrainment and rapid transport to the ocean. Based on these results we propose that these specific Upper Ordovician formations form a main source of IRD in HLs and hence infer an active role of the Hudson Strait paleo-ice flow in these events.

Keywords: Heinrich Layer; Biomarker; Organic geochemistry; Hudson Strait; Ordovician source rock; Paleozoic

Highlights:

- Screening of Paleozoic rocks from Canada for biomarker signature
- Compared with biomarker signature of Heinrich Layers in N. Atlantic
- Late Ordovician strata from Southampton and Baffin Islands have “Heinrich-type” signature
- Consistent with these formations being a source of IRD in Heinrich Layers

1. Introduction

Heinrich Events (HEs) are among the most dramatic examples of millennial-scale climate variability of the last glacial cycle (e.g., Heinrich, 1988; Bond et al., 1992; Hemming, 2004). First described at the Dryack Seamount in the eastern North Atlantic (Heinrich, 1988), the partial collapse of the continental ice sheets around the North Atlantic during HEs allowed ice-rafted debris (IRD) and finer mineral fractions (Andrews, 2000) to become widespread in sediments of the glacial North Atlantic north of $\sim 40^\circ\text{N}$; Heinrich Layers (HLs) (e.g., Heinrich, 1988; Bond et al., 1992; Hemming, 2004).

One of the key issues in research related to HEs has been the development and application of specific provenance indicators that aid in recognition of probable source areas and rock formations for the sedimentary inventory of HLs (e.g., Gwiazda et al., 1996; Farmer et al., 2003; Hemming, 2004; Rashid and Grosjean, 2006; Peck et al., 2007; Small et al., 2013). Mostly petrographic, inorganic, and bulk geochemical approaches have been applied to understand the provenance of HLs, allowing investigators to infer the age and isotopic composition of either bulk sediments, the fine ($<63\ \mu\text{m}$) fraction, or individual IRD grains (see review in Hemming, 2004). Based on this work as well as the observed decrease in abundance of IRD with increasing distance from North America, Paleozoic bedrock in the Hudson area of northern Canada has been suggested as the major source for IRD in HLs. However, it has been difficult to link specific HEs to individual rock formations.

Lately a growing body of work has demonstrated that erosion of ancient organic matter contained within rock formations during HEs caused HLs across the Labrador Sea and North Atlantic to have a distinct biomarker signature rich in aromatic/petrogenic compounds, indicating a Paleozoic origin (Rosell-Melé et al., 1997; Rashid and Grosjean, 2006; Naafs et al., 2011; Nicholl et al., 2012; Naafs et al., 2013a; Naafs et al., 2013b; Pearce et al., 2015). The same biomarker signature is also found within Heinrich(-like) Layers as old as 640 ka (Stein et al., 2009; Naafs et al., 2011; Naafs et al., 2013b). Within this context, it is crucial that the original biomarker signature of the source rock is retained within IRD found in marine sediment cores as shown by Parnell et al. (2008). Similar to other inorganic characteristics of HLs (Bond et al., 1992), the abundance of this “petrogenic” type of organic matter in HLs decreases with increasing distance from North America, suggesting a source in northern Canada (Naafs et al., 2013b).

However, so far it remains unknown what Paleozoic strata form the specific source of the petrogenic compounds and whether they are limited to the Hudson area alone. Potentially they could be used as source-specific tracers as proposed by Rashid and Grosjean (2006). However, Paleozoic bedrock can be found south of Hudson Bay (e.g. St. Lawrence estuary) and in the Canadian Arctic (Barton et al., 2003). For example, Parnell et al. (2007a) demonstrated that mature/aromatic compounds are also present in glacial sediment in Baffin Bay and can be found in Paleozoic rocks from the Canadian Arctic islands. In addition, the St. Lawrence region has been

suggested as an additional source of IRD during the last glacial (Bigg and Wadley, 2001; Watkins et al., 2007).

Here we analyze samples from various Paleozoic outcrops from across the former eastern margin of the Laurentide ice sheet for their biomarker signature. Using the biomarker signature of these Paleozoic source rocks in combination with that previously found in HLs (Naafs et al., 2013b), we aim to identify the source of the distinct biomarker signature found in HLs. Identifying the source can provide crucial evidence about the origin of icebergs calved during HEs, which is pivotal for our understanding of this type of millennial-scale climate variability.

2. Material and methods

2.1 Materials

We obtained a total of 34 samples from four outcrops across the former eastern margin of the Laurentide ice sheet (Table 1). Six samples came from Anticosti Island, located in the Gulf of St. Lawrence (Fig. 1). The Gulf of St. Lawrence was characterized by a fast-flowing Laurentian channel ice stream, evidenced by glacially-megalineated limestone terrain at Anticosti Island (Eyles and Putkinen, 2014). The carbonates from the Ellis Bay and Becscie formations (Fms) span the uppermost Ordovician and Lower Silurian and are representative for the Paleozoic carbonates at the southern margin of the Laurentide ice sheet (Jones et al., 2011), with low TOC values (<1 wt%) (Table 1).

Nine samples came from Cape Phillips Fm at the Twilight Creek Section on Bathurst Island that spans the Lower Silurian (Noble et al., 2005). Bathurst Island is located in the Canadian Arctic Archipelago (Fig. 1) and these samples are representative of the Paleozoic carbonates in the high Canadian Arctic. Although not as organic rich as the oil shales from Southampton and Baffin Islands, these samples have TOC values in the range of 1-3 wt% (Table 1).

A total of 15 samples (Table 1) came from the Red Head Rapids Fm exposed at Cape Donovan on Southampton Island at the entrance to the Hudson Bay. Southampton Island played an important role in controlling the location of the main ice streams of the Laurentide ice sheet (Ross et al., 2011). The Red Head Rapids Fm has a Late Ordovician (Richmondian) age and contains three intervals of organic rich oil-shales (TOC values as high as 35 wt%), interbedded with thick limestone and dolomite sequences (Zhang, 2008, 2011).

Five samples came from southern Baffin Island (Table 1), covering the Upper Ordovician Amadjuak and possible Forster Bay Fm. On Baffin Island the lower part of the Amadjuak Fm is characterized by an interbedded 2m thick black shale and limestones, while the upper part mainly consist of (weathered) limestones (Zhang, 2012). The black shale in the Amadjuak Fm is characterized by TOC values as high as 15 wt% and its stratigraphic position is lower than the lower oil shale found in the Red Head Rapids Fm on Southampton Island (Zhang, 2012). The Forster Bay Fm is less well defined at southern Baffin Island and only present as

scattered pieces of dolomitic limestone rubbles, which are similar to the those in the lower part of the Red Head Rapids Fm on Southampton Island (Zhang, 2012). Both the Amadjuak and the possible Forster Bay Fms are Late Ordovician in age (Zhang, 2012). Importantly, the Upper Ordovician strata sampled on Southampton and Baffin Islands are representative of the bedrock geology of the majority of the Hudson Strait (Sanford and Grant, 1998).

2.2 Methods

The surfaces of all rock samples were cleaned with water and acetone or dichloromethane to remove any attached material and external organic contamination. Samples were then crushed to powder and homogenized using a ball mill. For the samples from the Red Head Rapids Fm, between 3 and 10 grams of each sample were extracted with dichloromethane, using accelerated solvent extraction (Dionex ASE 200, 100 °C and 1000 psi for 5 min) at the AWI. The other samples were processed at the University of Bristol, where between 16 and 35 grams of each sample were extracted for 24 hrs with dichloromethane/methanol (2:1 volume) using a Soxhlet extractor. For most samples the total lipid extract was separated into three fractions using liquid chromatography and successively eluting hexane (3 ml), hexane/dichloromethane (3:1, 4 ml), and dichloromethane/methanol (2:1, 4 ml) over a 4 cm long silica gel column. This yielded a saturated hydrocarbon, aromatic, and polar fraction, respectively. After drying under a gentle nitrogen flow, the samples were

re-dissolved in hexane and analyzed. At AWI, a LECO Pegasus III time-of-flight mass spectrometer (TOF-MS), interfaced to an Agilent 6890 gas chromatograph (GC) was used for analysis (Hefter, 2008). At the University of Bristol, samples were analysed using a Thermoquest Finnigan GC coupled to a Thermoquest Finnigan MS detector. The detector was operated with an electron ionisation (EI) source (70 eV) and a scanning range of 50 – 650 Daltons. The GC was fitted with a silica capillary column (50 m x 0.32 mm internal diameter) coated with a CPSil-5CB stationary phase (dimethylpolysiloxane). Helium gas was used as the mobile phase. Samples were injected on-column (1 µl) at 70 °C. After one minute the oven temperature was increased to 130 °C at a rate of 20 °C/min, and then to 300 °C at a rate of 4 °C/min. The oven was held at 300 °C for 25 minutes. Although the sensitivity of the GC-TOF/MS is higher compared to the GC-MS system, re-analyses of samples from the Red Head Rapids Fm using the GC-MS system gave similar results. Laboratory blanks that underwent the same procedures as the rock samples indicated the absence of any of the investigated compounds.

2.3 Data analysis

A principle component analysis (PCA) was used to create a statistical background to compare the biomarker signature of the different outcrops to that of HLs. For this purpose we used the XLSTAT software, which is available online at <http://www.xlstat.com/>. For the PCA we selected 7 biomarker ratios that reflect the diversity of the different sources (see

supplementary information) from the biomarker signature of the 34 outcrop samples. These were combined with the biomarker ratios of IRD-layers from sediment cores in the Labrador Sea and North Atlantic (IODP Sites 1303, 1305, 1308, and U1313) (Naafs et al., 2013b).

3. Results

3.1 Anticosti Island (Ellis Bay and Becscie Fms)

The biomarker signature of the samples from Anticosti Island was characterized by abundant *n*-alkanes (C₁₆ – C₃₉, Fig. 2a). The carbon preference index (CPI) of the long-chain *n*-alkanes, calculated following Bray and Evans (1961), varied between 1 and 2 for all samples.

Pristane and phytane were present in all samples, but were not abundant. Hopanes were abundant and dominated by the mature 17 α (H), 21 β (H) isomers (Fig. 3a), especially the C₂₉ and C₃₀ homologues, as well as minor amounts of C₂₉-C₃₁ 17 β (H),21 α (H) hopanes. The ratio between 17 α -22, 29, 30-trisnorhopane (Tm) and 18 α -22, 29, 30-trisnorneohopane (Ts), Ts/(Ts+Tm) (Seifert and Michael Moldowan, 1978), varied between 0.1 and 0.6 (see supplementary information). The C₃₄ hopanes did not dominate over the C₃₃ homologues. Most samples contained triaromatic steroids (Fig. 4a), identified based on their characteristic *m/z* 231 fragment ion and relative retention times (Riolo et al., 1986). Small amounts of C₃₂-C₃₃ benzohopanes (Fig. 3a) and C₂₉-C₃₁ D-ring monoaromatic 8,14 secohopanoids (Fig. 5a), identified based on published mass spectra (Hussler et al., 1984a; Hussler et al., 1984b), were also present within

some samples. Aromatic compounds such as Palae- and isorenieratane, C-ring monoaromatic steroids, C₃₄-C₃₅ benzohopanes, and C₃₂-C₃₅ D-ring monoaromatic 8,14 secohopanoids, were not detected in the samples from Anticosti Island.

3.2 Bathurst Island (Cape Phillips Fm)

The biomarker distribution of the samples from Bathurst Island was dominated by *n*-alkanes (C₁₅ – C₃₇, Fig. 2b) without a clear odd over even predominance (CPI ~ 1). Pristane and phytane were abundant and dominated over the C₁₇ and C₁₈ *n*-alkanes, especially in the lower part of the section. A number of samples contained traces of triaromatic steroids (Fig. 4b), C₂₉-C₃₃ 17 α (H),21 β (H) hopanes (Fig. 3b), and possibly trace amounts of C₂₉ and C₃₀ D-ring monoaromatic 8,14 secohopanoids (Fig. 5b). Where present, Ts/(Ts+Tm) ratios were > 1-2. Palaerenieratane and aryl isoprenoids, identified based on published relative retention times and spectra (Koopmans et al., 1996), were present in the bottom part (8-50m) of the section (Fig. 6b). Isorenieratane, C-ring monoaromatic steroids, C₃₄-C₃₅ 17 α (H),21 β (H) hopanes, benzohopanes, and C₃₁-C₃₅ D-ring monoaromatic 8,14 secohopanoids, were not detected in the samples from the Cape Phillips Fm at the Twilight Creek Section.

3.3 Southampton Island (Red Head Rapids Fm)

The organic rich shales (TOC of up to 28 %, Table 1) and organic poor carbonates (TOC as low as 0.1 %) in the Red Head Rapids Fm contained a

wide-array of organic compounds (Fig. 8). The *n*-alkane distribution (Fig. 2d) lacked a clear odd over even predominance with a CPI between 1 and 2. Pristane and phytane were abundant and dominated over the C₁₇ and C₁₈ *n*-alkanes. Phytane was more abundant than pristane in most samples.

Importantly within the context of this study, the oil shales were characterized by a high abundance of petrogenic compounds. C-ring monoaromatic steroids (Fig. 7b) and triaromatic steroids (Fig. 4d), identified based on their characteristic *m/z*'s 253 and 231 (Riolo et al., 1986), were found in almost all samples (Fig. 8). The tri- and monoaromatic steroids were dominated by the C₂₈(S) homologues (Figs. 4d and 7b). In addition, isorenieratane and palaerenieratane and related compounds such as aryl isoprenoids, identified based on the characteristic *m/z* 133+134 fragment ions and published mass spectra and relative retention times (Koopmans et al., 1996), were present (Fig. 6c). Hopanes, benzohopanes, and secohopanoids were present within the oil-shales, but a more significant distribution was found within the carbonates (limestones and dolomites) of the Red Head Rapids Fm. (Fig. 8). The hopane distribution was dominated by the mature 17 α (H),21 β (H)-isomers and the C₃₄ hopane dominated over the C₃₃ and C₃₅ homologues (Figs. 3d). The C₃₄ over C₃₃ hopanoid dominance was the most pronounced within the carbonates (Fig. 8, and supplementary information). Also for the benzohopanes (Fig. 3d) and secohopanoids (Fig. 5d), the C₃₄ homologues dominated over the C₃₃ and C₃₅ hopanoids.

264

265 3.4 Baffin Island (Amadjuak and possible Forster Bay Fms)

266 Samples from the Amadjuak Fm. contained a biomarker distribution that
267 is comparable to that found in the Red Head Rapids Fm from
268 Southampton Island. The *n*-alkane distribution (Fig. 2c) lacked a clear odd
269 over even predominance and the CPI of all samples was close to 1.
270 Pristane and phytane were abundant, dominating over the C₁₇ and C₁₈ *n*-
271 alkanes. The samples contained C-ring monoaromatic steroids (Fig. 7a),
272 triaromatic steroids (Fig. 4d), and isorenieratane and palaerenieratane as
273 well as their derivatives (Fig. 6a), almost identical to those found in the
274 shales of the Red Head Rapids Fm on Southampton Island. These samples
275 contained relatively few hopanoids. The more carbonate rich sample from
276 the possible Forster Bay Fm contained the same aromatic compounds as
277 well as abundant hopanes and hopanoids with a clear C₃₄/C₃₃ dominance
278 (Fig. 3c).

279

280 4. Discussion

281 4.1 Depositional environment Hudson area during the Late 282 Ordovician

283 The higher concentration of monoaromatic steroids compared to
284 triaromatic steroids as well as dominance of C₂₆-C₂₈ over C₂₀-C₂₂
285 homologues for both mono- and triaromatic steroids suggests that the
286 samples from Southampton and Baffin Island have a relatively low

thermal maturity (Palacas et al., 1986), in-line with the low T_{\max} values (Zhang, 2008, 2012).

Koopmans et al. (1996) already identified palaerenieratane, isorenieratane, and numerous diagenetic and catagenetic products of carotenoids in one sample from the Boas River oil shale from Southampton Island. Zhang (2008, 2011) redefined the stratigraphy on Southampton Island so that the lower black shale unit in the Red Head Rapids Fm that we analyzed is at the same stratigraphic position as that of the Boas River oil shale. Interestingly, our results indicate that the biomarker distribution is different between the lower (“Boas River”) oil shale and the middle (“Sixteen Mile Brook”) oil shale in the Red Head Rapids Fm. The lower oil shale is characterized by abundant C_{15} - C_{27} arylisoprenoids and C_{21} - C_{23} diarylisoprenoids. In the middle oil shale these arylisoprenoids are less abundant compared to palae- and isorenieratane and diarylisoprenoid are absent. In this context, the fact that we find abundant C_{15} - C_{27} arylisoprenoids and C_{21} - C_{23} diarylisoprenoids in the samples from the Amadjuak and the possible Forster Bay Fms on Baffin Island suggests that these are not the equivalent of the middle (Sixteen Mile Brook) oil shale found on Southampton Island, but likely correspond to the lower (“Boas River”) oil shale.

The presence of palae-, isorenieratane, and related (di-) aryl isoprenoids (elevated $\delta^{13}C$ with values between -18.9 and -17.2 ‰ (Koopmans et al., 1996)) is indicative of a marine source rock deposited

under euxinic conditions that reached the photic zone (Summons and Powell, 1986; Koopmans et al., 1996; Overmann, 2008). The overall dominance of long-chain (C₁₈-C₂₂) arylisoprenoids over short chain (C₁₃-C₁₇) arylisoprenoids suggests that the anoxic phases were persistent and not episodic (Schwark and Frimmel, 2004).

Although the organic rich shales contain high concentrations of aromatic compounds, the thick dolomite and limestone layers are characterized by abundant hopanoids with a clear C₃₄ over C₃₃ dominance. This is in agreement with other studies, which found that D-ring monoaromatic 8,14-secohopanoids and benzohopanes form during diagenesis from microbial hopane precursors and are particularly abundant within carbonate-rich formations (Hussler et al., 1984b; Jiang et al., 2001).

4.2 Identification of the source of IRD in HLs

Studies of the biomarker signature of HLs in the Labrador Sea and North Atlantic demonstrated that these detrital layers are characterized by a unique distribution that points to Paleozoic bedrock in the Hudson area as source (Rosell-Melé et al., 1997; Rashid and Grosjean, 2006; Naafs et al., 2013b). The presence of exotic compounds such as tri- and monoaromatic steroids, palaerenieratane/isorenieratane-derivatives, and the dominance of mature ($\alpha\beta$) hopanoid isomers cannot be related to *in situ* production within the water column or sediment. For example, palaerenieratane is only known from rocks that are older than ~ 250 Myrs (French et al., 2015) and there is no extant organism known that produces this

compound. Similarly, the isomerization of hopanoids to thermally more stable $\alpha\beta$ -isomers and aromatisation of steroids in marine sediments generally occurs during burial at great depth and on geological ($> 10^6$ yr) time scales (Mackenzie et al., 1980; Mackenzie et al., 1981). As such the presence of these biomarkers in late Quaternary HLs has to result from glacial erosion and transport of ancient organic matter contained in Paleozoic rock formations.

The biomarker signatures of the Ordovician Red Head Rapids Fm on Southampton Island and Amadjuak and possible Forster Bay Fms on Baffin Island are remarkably similar to that of the HLs in the North Atlantic with the abundance of palaerenieratane, isorenieratane and derivatives (Fig. 6d), $C_{28}(S)$ dominance in the tri- (Fig. 4e) and monoaromatic steroids (Fig. 7c), and the C_{34} over C_{33} hopanoid dominance (Figs. 3e and 5e).

The PCA demonstrates that the first two factors explain 73% ($F_1 = 57$ and $F_2 = 16.2$ %) of the variance (Fig. 9) and clearly separates the different outcrops (see supplementary information for factor loadings). The samples from Bathurst and Anticosti Island have positive factors scores for F_1 , while those from Baffin and Southampton Islands have negative scores. Samples from Bathurst and Anticosti Islands that contain palaerenieratane are separated along F_2 from those that do not contain this compound. The samples from Baffin and Southampton Islands plot closely together and are distinctly different from Bathurst and Anticosti Island. Importantly, HLs 5-1 plot directly on top of the samples from

Baffin and Southampton Island (Fig. 9), indicating an identical biomarker distribution. We therefore argue that the similarity in biomarker signatures is consistent with these formations being a major source of IRD during HEs

Rashid and Grosjean (2006) postulated that the source rock of the ancient organic matter in HLs has to meet two criteria: the presence of isorenieratane and dominance of C₃₄ over C₃₃ hopanes. Only the Upper Ordovician formations from the Hudson area (Southampton and Baffin Islands) meet these criteria. Besides the striking comparison between the biomarker signature of the Upper Ordovician strata from Southampton and Baffin Islands and HLs in the North Atlantic and Labrador Sea (Fig. 9), the presence of thick limestone and dolomite packages within the Upper Ordovician strata is in agreement with the high abundance of detrital carbonate in HLs (e.g., Andrews and Tedesco, 1992; Bond et al., 1992) and further supports our hypothesis that these formations contributed to the IRD found in HLs in the Labrador Sea and North Atlantic IRD-belt.

It is important to stress that the Upper Ordovician strata from Southampton and Baffin Islands we analyzed are the exact same strata that make up the majority of the current bedrock of the Hudson Strait. The few drillings available from the 1980s indicate that organic rich shales (TOC up to 12.78 wt%) are present in the Hudson Strait at shallow depth (< 1.5 m) (Zhang, 2013). Furthermore, Zhang (2008) suggested that the same formations and organic rich shales can be found throughout the

Hudson Bay based on the gamma ray logs from Hudson Bay offshore, which is now supported by additional data from onshore cores drilled in Manitoba and Ontario (Armstrong and Lavoie, 2010; Nicolas and Lavoie, 2012). In fact at these locations the oil shale can be more than 10m thick. We argue that the similarity in biomarker signature of the samples from Southampton Island and Baffin Island indicate a high degree of chemical homogeneity in these formations across the Hudson area. These formations outcrop across Hudson Bay and Hudson Strait with dip angles from 30 to 80° (Sanford and Grant, 1998) and therefore can continuously supply material for repeated erosion by the waxing and waning of the Laurentide ice sheet during the Pleistocene. Even so, successive erosion by the waxing and waning of the Laurentide ice sheet during the Pleistocene might have removed part of outcrops and these formations might have been more widespread during previous glacials.

The Hudson Ice Stream drained a large part of the Laurentide ice sheet and the catchment consisted of number of ice streams potentially extending all the way into the western Hudson Bay (far inside the Laurentide ice sheet) (Andrews and MacLean, 2003; Ross et al., 2011). Thus the Upper Ordovician formations are ideally positioned to be entrained by paleo-iceflows that produced large numbers of sediment loaded icebergs during calving events that subsequently traveled far into the North Atlantic.

4.3 Supporting evidence

Over the past two decades, a large number of studies used inorganic and bulk geochemical approaches to infer the source of IRD in HLs (e.g., Grousset et al., 1993; Revel et al., 1996; Grousset et al., 2001; Farmer et al., 2003; Hemming, 2004; Peck et al., 2007; Hodell and Curtis, 2008; Andrews et al., 2012; Downing and Hemming, 2012). Although a wide array of tracers has been used (reviewed by Hemming, 2004), the Nd, Sr, and stable $\delta^{18}\text{O}$ isotopic composition of HLs are among the most characteristic. To test whether the Upper Ordovician strata on Southampton and Baffin Islands also fit within the established context of inorganic properties of HLs, we determined the Nd, Sr, and stable $\delta^{18}\text{O}$ isotopic composition of carbonate and shale samples from Southampton Island.

Hodell and Curtis (2008) showed that detrital carbonate grains from different HLs have low $\delta^{18}\text{O}$ values that varied between -3 and -10 ‰, with an average value of -5.6 ± 1.5 ‰. The $\delta^{18}\text{O}$ values we obtained for the carbonates from the Red Head Rapid Fm are similarly low (Table 2) with an average value of -8.2 ± 0.27 ‰ ($n = 3$).

Grousset et al. (1993) first showed that IRD in HLs have low ϵ_{Nd} values in the range of -10 to -20 and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios around 0.73, suggestive for a source in northern Canada. Later studies confirmed these results (e.g., Farmer et al., 2003; Hemming, 2004). The ϵ_{Nd} values and $^{87}\text{Sr}/^{86}\text{Sr}$ of the Red Head Rapids Fm on average are -15.4 ± 1.1 ($n = 3$) and 0.7110 ± 0.0009 ($n = 3$) for the shales and -11.6 ± 1.2 ($n = 3$) and 0.7081 ± 0.00002 ($n = 3$) for the carbonates respectively (Table 2). Although these

values are comparable to those found for IRD in HLs, the ϵ_{Nd} values of the carbonates are at the higher end of those found in HLs. This is likely due to the fact that although the presence of detrital carbonate is a key-feature of HLs in the North Atlantic, studies involving ϵ_{Nd} values and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios normally involve carbonate-free IRD as sample are treated with acid prior to analysis to remove biogenic carbonate. Thus, the ϵ_{Nd} values and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios reported from HLs are not representative for carbonates. Future studies should determine the ϵ_{Nd} values and especially $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of individual carbonate grains from HLs.

In addition, the range of the inorganic geochemical signature reported for HLs is larger than that found in our sample set from Southampton Island. Although this might reflect spatial heterogeneity within these Upper Ordovician formations not represented in our limited sample set, it likely indicates a contribution of ice-rafted debris derived from other locations with a distinct inorganic geochemical signature (e.g., European sourced IRD). The data reported here from the Upper Ordovician formations on Southampton Island likely represents the Hudson Strait end-member.

Although we did not explore each inorganic geochemical approach that has previously been used to infer the source of IRD in HLs, our results do indicate that key-inorganic geochemical characteristics of the Upper Ordovician strata are similar to those found for HLs, providing further supporting evidence for our hypothesis that these specific Upper Ordovician strata are a main source of IRD in HLs.

455

456 **4.4 Comparison with published biomarker signatures**

457 Relatively few studies have used biomarkers to trace IRD in marine
458 sediments. Parnell et al. (2007a; 2007b) showed that Paleozoic formations
459 from Devon and Cornwallis Islands (Canadian Arctic) contained
460 triaromatic steroids, *n*-alkanes, and hopanes, although the hopanes lacked
461 a clear C₃₄ over C₃₃ dominance. Together with the fact that we find
462 triaromatic steroids in samples from Anticosti Island (although at much
463 lower concentrations compared to the oil shales from Southampton and
464 Baffin Islands), these results indicate that triaromatic steroids are less
465 source-specific compared to the other petrogenic compounds.

466 Obermajer et al. (2010) determined the biomarker signature of a
467 number of Devonian, Silurian, and Ordovician rocks from the Canadian
468 Arctic Archipelago. These samples contained little aromatic compounds
469 and almost all samples have pristane/phytane ratios greater than one. In
470 addition, samples from the Canadian Arctic Archipelago (including a
471 sample from the Cape Phillips Fm) all lacked a clear C₃₄ over C₃₃ hopane
472 dominance, similar to our results from the Cape Phillips Fm at Bathurst
473 Island. These results differ from those found in the samples from
474 Southampton and Baffin Island and HLs that are characterized by
475 abundant aromatic compounds and pristane/phytane ratios < 1.

476 Lastly, the mature *n*-alkane distribution found in all Paleozoic
477 rocks with CPI values around one support the idea that the input of re-
478 worked *n*-alkanes to the North Atlantic is mainly controlled by ice-rafting

intensity (Villanueva et al., 1997), but this signal is not source-specific. The higher CPI found in HLs reflects the additional input of aeolian derived higher plant waxes during Quaternary glacials (López-Martínez et al., 2006; Naafs et al., 2012).

4.5 Implications

Our results demonstrate that the biomarker signature of the Upper Ordovician strata from Southampton and Baffin Island differs from that of other bedrock geology that the Laurentide ice sheet covered during glacials. Of the outcrops analyzed here, only the biomarker signature of the Upper Ordovician strata from the Hudson Bay area is comparable to that found in HLs. The identification for the first time of specific rock formations in the Hudson Bay area as a main source of the sedimentary occurrence of petrogenic compounds can help to shed more light on the processes associated with the (partial) collapse of the Laurentide ice sheet.

For example, the advantage of biomarkers over classical $>63\ \mu\text{m}$ IRD studies is that the biomarker approach relies on extraction from bulk sediment samples and as such is sensitive to distal small-scale ice sheet collapse and outburst flood events not detected by classical IRD methods. We envision that using the petrogenic compounds in proximal sediment cores spanning the early Pleistocene has the potential to detect so-far unknown periods of ice sheet instabilities through the Hudson Strait of a smaller scale than the large Heinrich(-like) Events that appear to be restricted to the middle and late Pleistocene (Hodell et al., 2008; Naafs et

al., 2013b). In addition, the possibility to trace Heinrich Events using biomarkers in combination with other organic geochemical proxies such as the $U^{K_{37}}$ and/or TEX_{86} palaeothermometers or IP_{25} sea-ice biomarker allows for a detailed assessment of leads and lags in the climate system as both analyses can now be done on the exact same sample.

Previous studies argued whether HLs 6 and 3 represent classic HEs and ice rafting through the Hudson Strait or had a different source (e.g., Hemming, 2004; Rashid and Grosjean, 2006). The biomarker signature of HL 6, as well as low detrital carbonate layer 2 and detrital carbonate layer 6, is distinct from the other HLs and the Upper Ordovician formations from Southampton and Baffin Island (Fig. 9). This suggests a non-Hudson Strait source of IRD during these events. On the other hand, the biomarker signature of HL 3 in sediment cores from the Labrador Sea and center of the IRD-belt (Fig. 9) suggests that HE 3 did involve the ice-flow of the Hudson Strait. In addition, our results allow the previous identification of petrogenic compounds in H0 (Pearce et al., 2015) to specifically infer instability of the ice-flow in the Hudson Strait around the time of the Younger Dryas and not Baffin Bay as suggested previously (Andrews et al., 2012). Our results further confirm that the Laurentide outburst flood at the onset of the last interglacial (Nicholl et al., 2012) specifically involved the Hudson Strait. Lastly, our results suggest that the Canadian Arctic Archipelago was likely not a major source of IRD during HEs as the biomarker signature of those Paleozoic rocks differs from that found in HLs.

Our findings do not definitively prove that the Hudson Bay outcrops are the source of the material in all the Heinrich(-like) layers throughout the Quaternary. However, as Heinrich(-like) layers MIS 8, 10, 12, and 16 are characterized by a similar biomarker signature as the HLs of the last glacial (Naafs et al., 2013b), our results provide further evidence that an active paleo-ice flow was located within the Hudson Strait during previous glacials.

5. Conclusions

An important focus in research related to HEs has been the development of specific provenance indicators. Here we used organic biomarkers to trace the source of IRD in HLs. We analysed Paleozoic rocks from across the former eastern margin of the Laurentide ice sheet and show that from all formations analysed, only the biomarker signature of Upper Ordovician strata on Southampton and Baffin Islands is compatible with that found in HLs in the Labrador Sea and North Atlantic. In addition to the biomarker signatures, key-inorganic characteristics ($\delta^{18}\text{O}$, ϵ_{Nd} , and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios) of these strata are consistent with that found in HLs. The locations of these strata in and around the Hudson Strait are compatible with paleo-ice flow regimes through the Hudson Strait (Andrews and MacLean, 2003), allowing for easy entrainment and rapid transport to the North Atlantic. Based on these results we propose that the Upper Ordovician strata formed a main source of IRD during HEs of

the middle and late Pleistocene, indicating an active role of the Hudson Strait paleo-ice flow in these events.

6. Acknowledgements

We thank A. Mackensen for measuring the stable carbon and oxygen isotopic composition of the carbonates from the Red Head Rapids Fm. M. Frank is acknowledged for measuring the ϵ_{Nd} values and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of these samples as well as the shales. P. Noble and D. Jones are thanked for generously sharing samples from Bathurst (collected under NSF grant 9870431) and Anticosti Island. B.D.A.N. acknowledges funding by the DFG (grant NA 973/1-1) and a NWO Rubicon Grant. We also thank the associate editor E. Canuel and three anonymous reviewers for their comments and suggestions.

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Tables

Table 1; Overview of outcrop samples used in this.

Table 2; Inorganic geochemical parameters for selected samples from the

Red Head Rapids Fm on Southampton Island. n.d. = not

determined.

Figure Legends:

Figure 1; Map showing the IRD accumulation in the North Atlantic during the last glacial (modified after Ruddiman, 1977) together with the location of the cores in which the biomarker signature of HLs was determined.

Yellow dots represent the Paleozoic outcrop locations: (1) Ellis Bay and Becscie Fms, Anticosti Island; (2) Amadjuak and possible Forster Bay Fms, Baffin Island; (3) Red Head Rapids Fm, Southampton Island; and (4)

Cape Philips Fm, Bathurst Island. Black dots represent the locations of marine sediment cores: (A) HU90013-29; (B) IODP U1305; (C) IODP U1302/03; (D) EW9302-1JPC; (E) IODP U1308/609; (F) BOFS 5k; and (G) IODP U1313/607.

Figure 2; Mass chromatograms of m/z 71 depicting the distribution of n -alkanes and isoprenoids (pristane and phytane) typical for samples from (a) Anticosti Island, (b) Bathurst Island, (c) Baffin Island, (d) Southampton Island, and (e) a Heinrich Layer. CPI stands for Carbon Preference Index. Note that in North Atlantic sediments, aeolian dust is a major source of plant leaf waxes that contain n -alkanes with a $CPI > 1$ (Naafs et al., 2012).

Figure 3; Mass chromatograms of m/z 191 indicating the relative abundance and distribution of hopanes (black) and benzohopanes (red) in samples from (a) Anticosti Island, (b) Bathurst Island, (c) Baffin Island, (d) Southampton Island, and (e) a Heinrich Layer. C_{33}/C_{34} ratios of these hopanoids with a value < 1 indicate the dominance of the C_{34} hopanoids over C_{33} homologues.

Figure 4. Mass chromatograms of m/z 231 indicating the distribution of triaromatic steroids in samples from (a) Anticosti Island, (b) Bathurst Island, (c) Baffin Island, (d) Southampton Island, and (e) a Heinrich Layer. Carbon atom numbers and S/R isomers are indicated.

843

844 Figure 5. Mass chromatograms of m/z 365 representative for the
845 abundance of D-ring monoaromatic 8,14-secohopanoids in samples from
846 (a) Anticosti Island, (b) Bathurst Island, (c) Baffin Island, (d)
847 Southampton Island, and (e) a Heinrich Layer. Carbon atom numbers and
848 S/R isomers are indicated, as well as the C_{33}/C_{34} ratios of these compounds
849

850 Figure 6; Summed mass chromatograms of m/z 133+134 showing the
851 distribution of aryl-isoprenoids and carotenoids for samples from (a)
852 Baffin Island, (b) Bathurst Island, (c) Southampton Island, and (d) a
853 Heinrich Layer. P and I stand for palae- and isorenieratane, respectively.
854 These compounds were not detected in samples from Anticosti and
855 therefore not included in this figure.

856

857 Figure 7; Mass chromatograms of m/z 253 representing C-ring
858 monoaromatic steroids in samples from (a) Baffin Island, (b)
859 Southampton Island and (c) a Heinrich Layer. These compounds were not
860 detected in samples from Anticosti and Bathurst Islands and therefore not
861 included in this figure.

862

863 Figure 8; Variations in the different type of diagnostic (petrogenic)
864 compounds in the Red Head Rapids Fm on Southampton Island where
865 several oil shales are intercalated with limestones and dolomites. The
866 TOC content of each sample is given in the upper right corner of the m/z

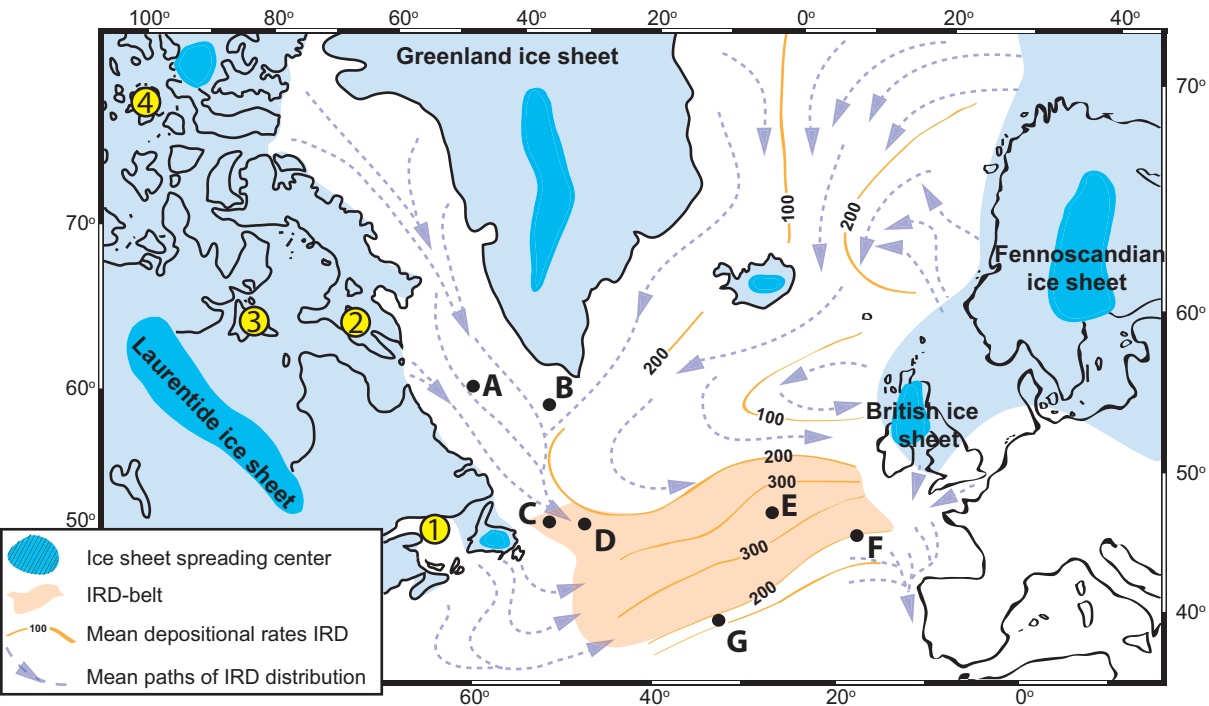
867 133+134 chromatograms (aryl-isoprenoids). m/z 231 = triaromatic
868 steroids, m/z 253 = C-ring monoaromatic steroids, m/z 191 = hopanes and
869 benzohopanes, m/z 365 = D-ring monoaromatic 8,14-secohopanoids.
870 Scaling factors are given in the upper left corner of each chromatogram to
871 provide a relative measure on the abundance of the compounds (i.e. the y-
872 axes all differ). In general, the compounds where the most abundant in
873 sample Z044-12 (scaling factor = 1).

874

875

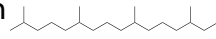
876 Figure 9: Principle component analysis (PCA) of the 34 rock samples and
877 IRD-layers from the Labrador Sea and North Atlantic (Naafs et al.,
878 2013b). For factor loadings and variables used see supplement.

879

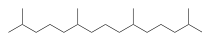


m/z 71

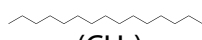
a) Anticosti 914-3.5 Ellis Bay Fm



Phytane

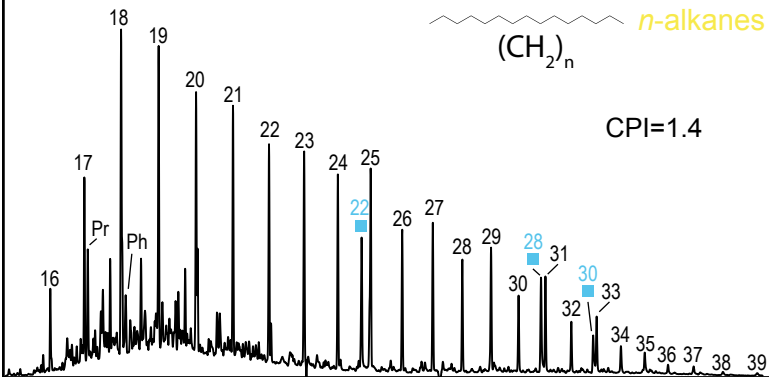


Pristane

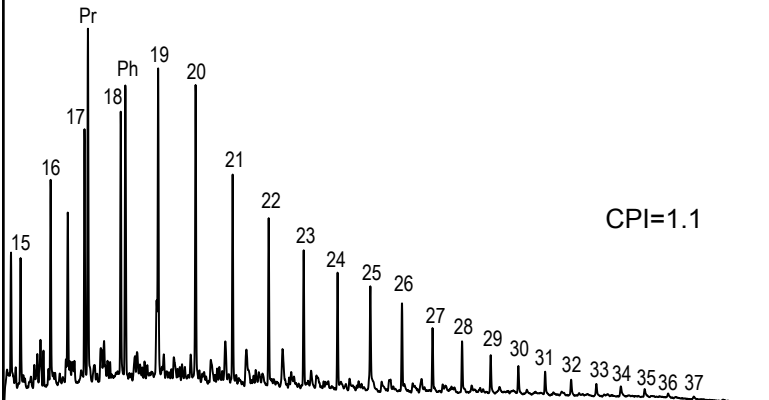


n-alkanes

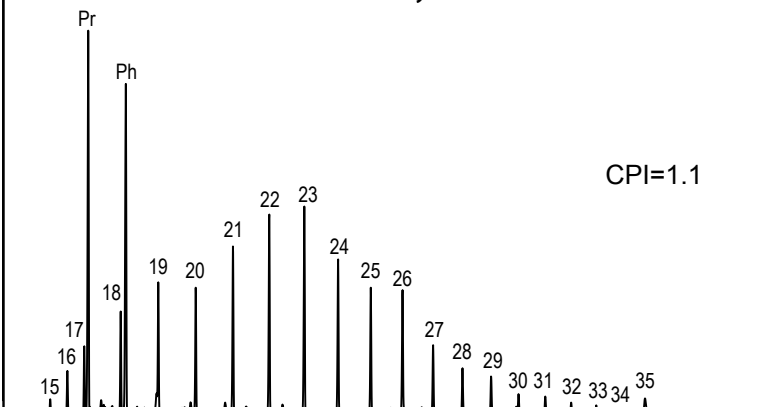
(CH₂)_n



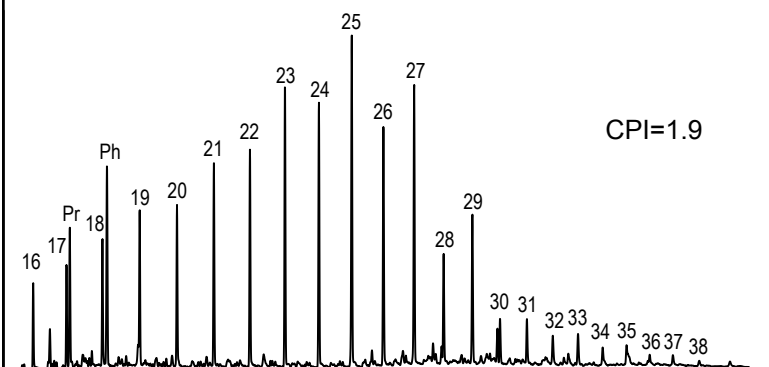
b) Bathurst TWC-18 Cape Philip Fm



c) Baffin 11SZ-14-01 Forster Bay Fm

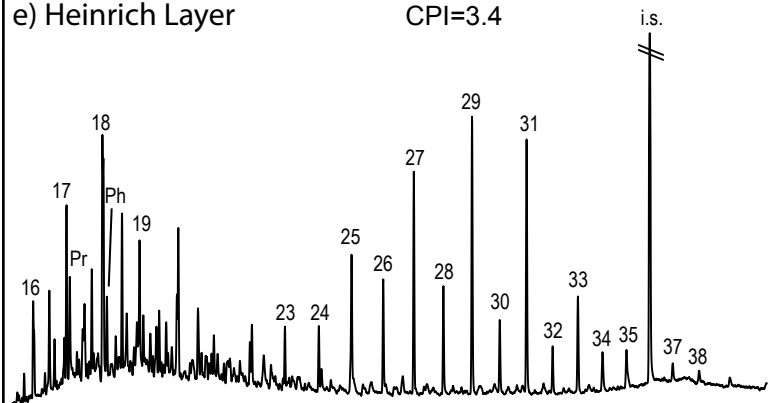


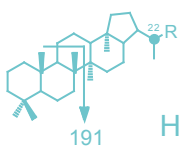
d) Southampton 07CYA-Z040-02 Red Head Rapids Fm



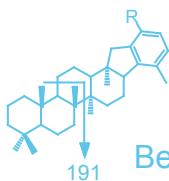
e) Heinrich Layer

CPI=3.4





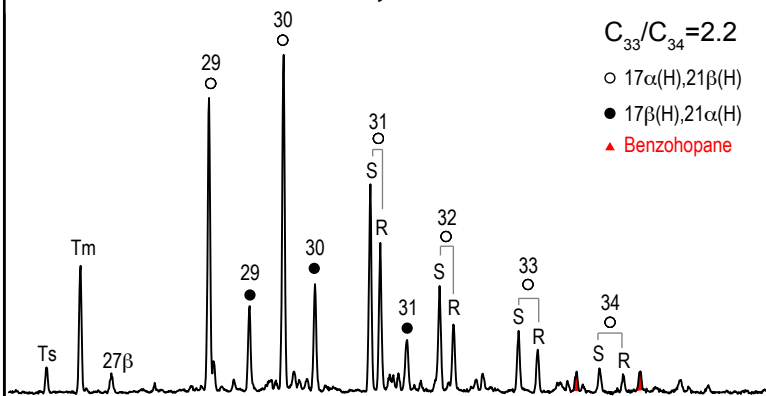
Hopanes



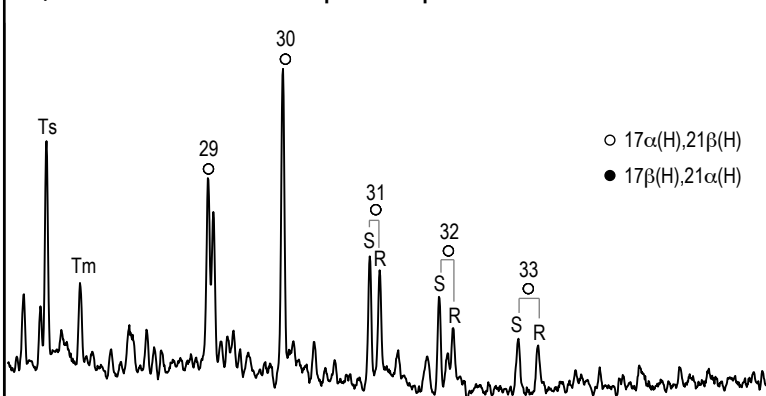
Benzohopanes

m/z 191

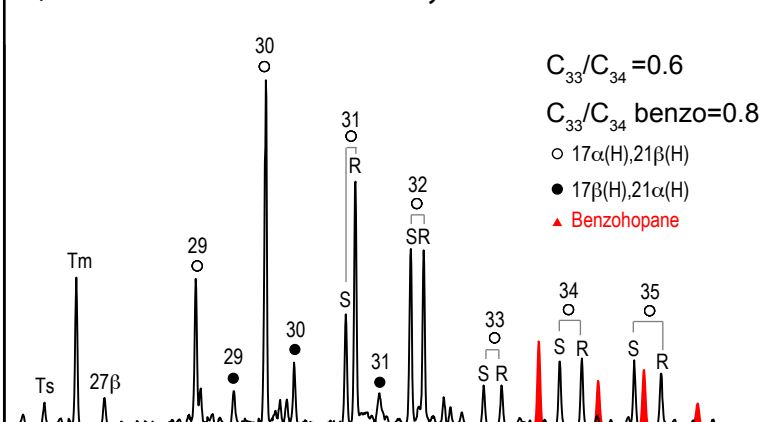
a) Anticosti 914-3.5 Ellis Bay Fm



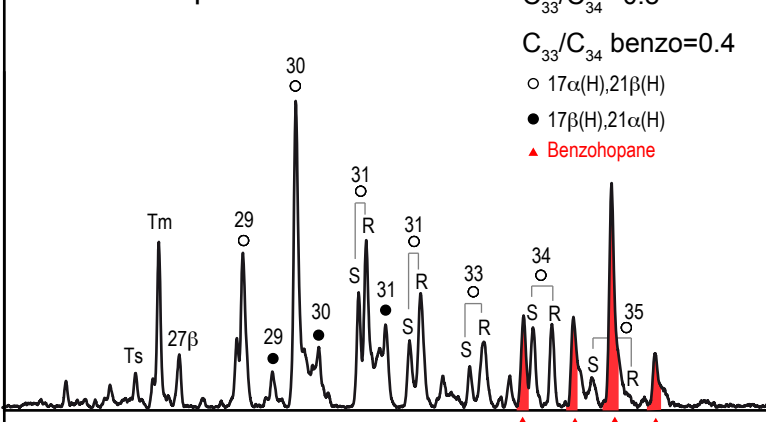
b) Bathurst TWC-18 Cape Philips Fm



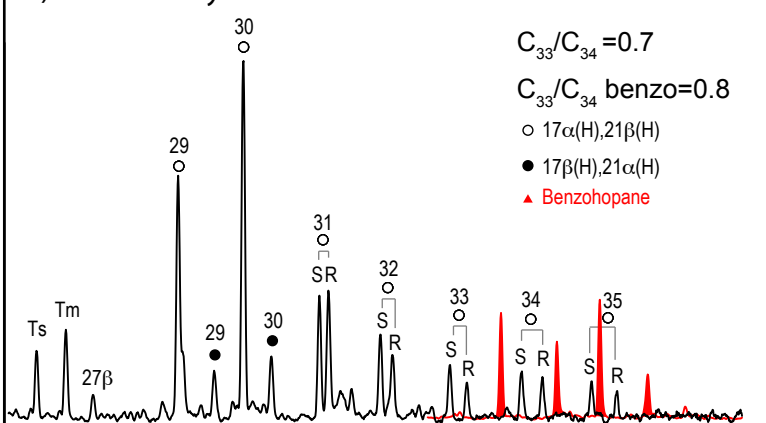
c) Baffin 11SZ-14-01 Forster Bay Fm

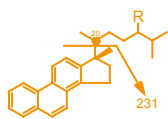


d) Southampton 07CYA-Z040-07
Red Head Rapids Fm



e) Heinrich Layer

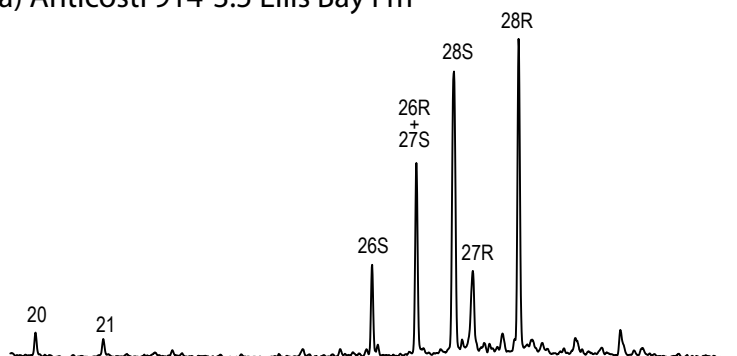




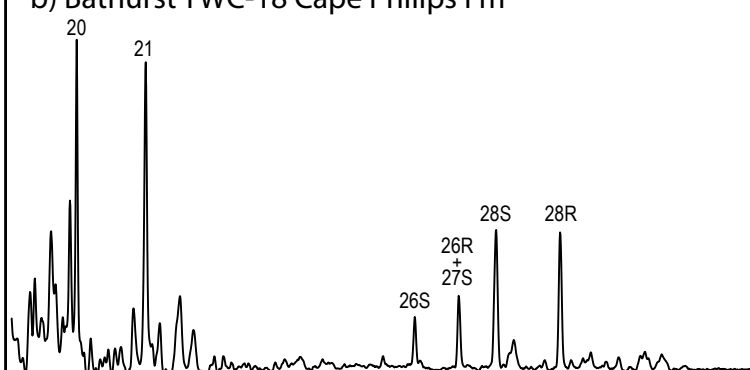
Triaromatic steroids

m/z 231

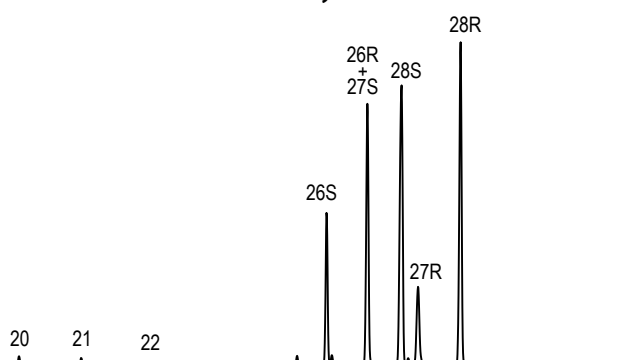
a) Anticosti 914-3.5 Ellis Bay Fm



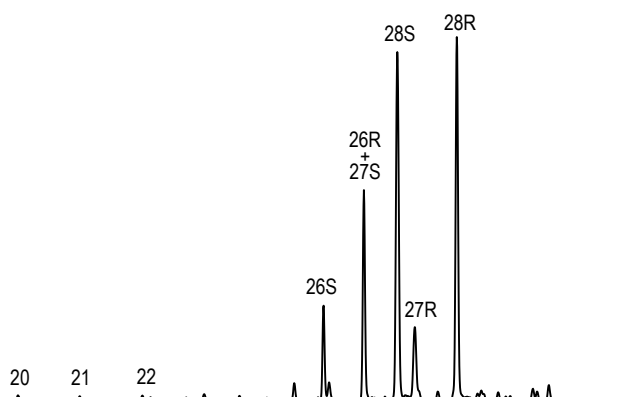
b) Bathurst TWC-18 Cape Philips Fm



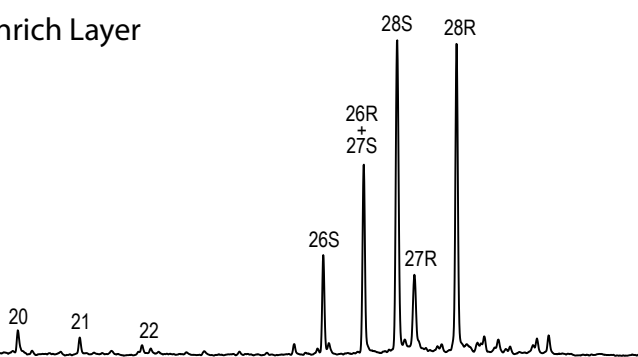
c) Baffin 11SZ-14-01 Forster Bay Fm

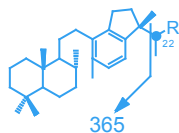


d) Southampton 07CYA-Z040-02 Red Head Rapids Fm



e) Heinrich Layer

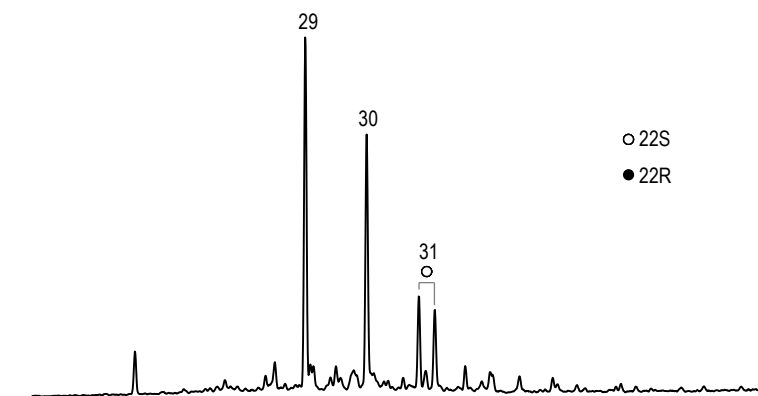




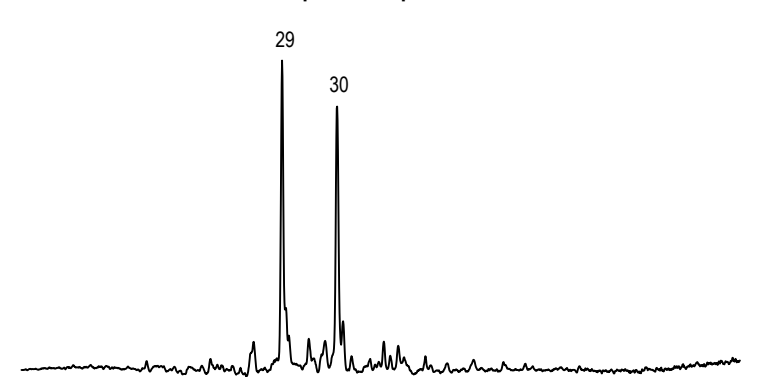
D-ring monoaromatic 8,14-secohopanoids

m/z 365

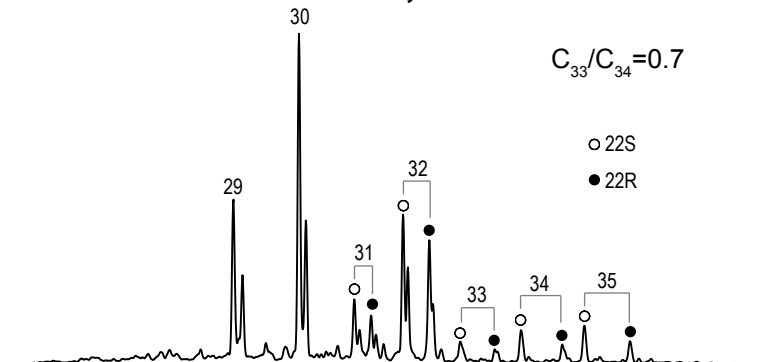
a) Anticosti 914-3.5 Ellis Bay Fm



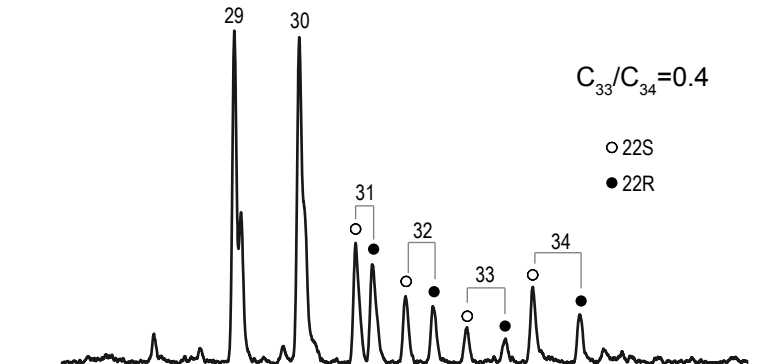
b) Bathurst TWC-18 Cape Philips Fm



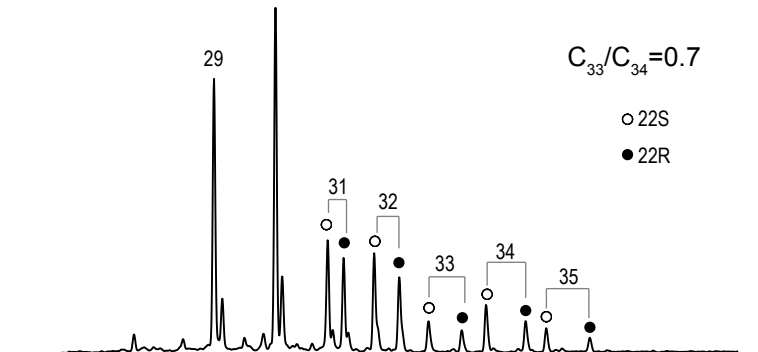
c) Baffin 11SZ-14-01 Forster Bay Fm

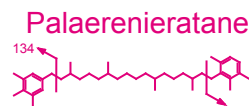
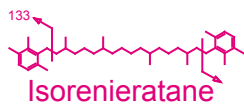


d) Southampton 07CYA-Z040-07 Red Head Rapids Fm



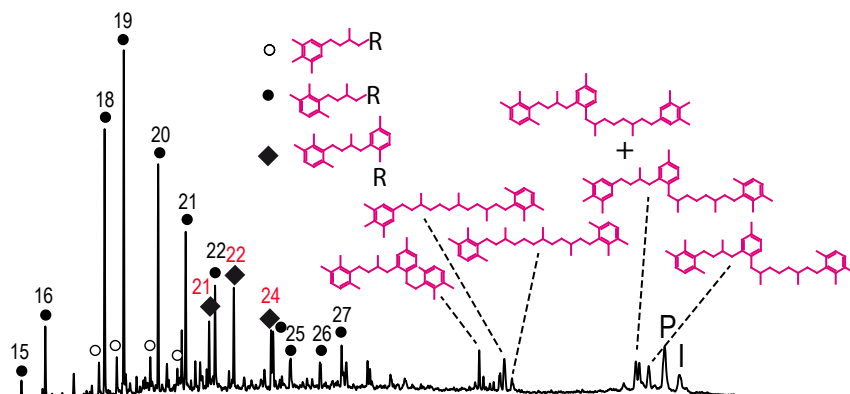
e) Heinrich Layer



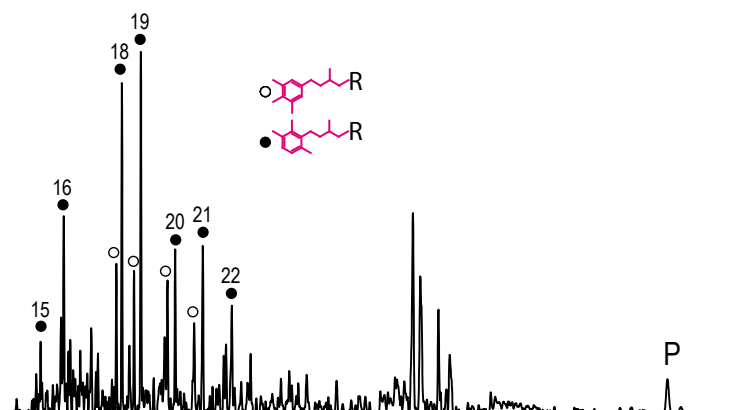


m/z 133+134

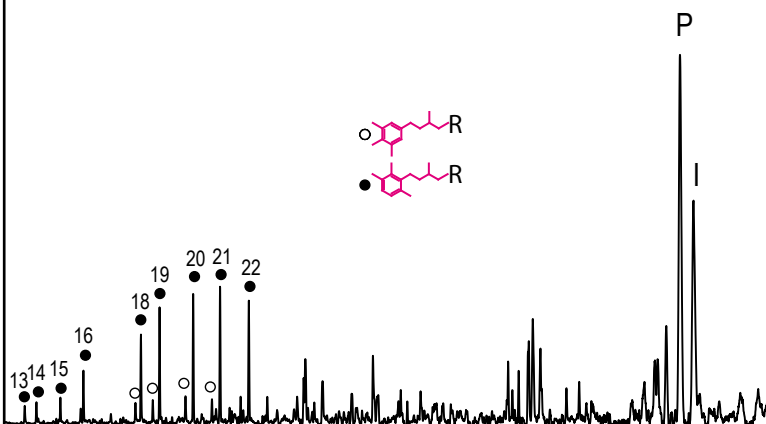
a) Baffin 11SZ-14-01 Forster Bay Fm



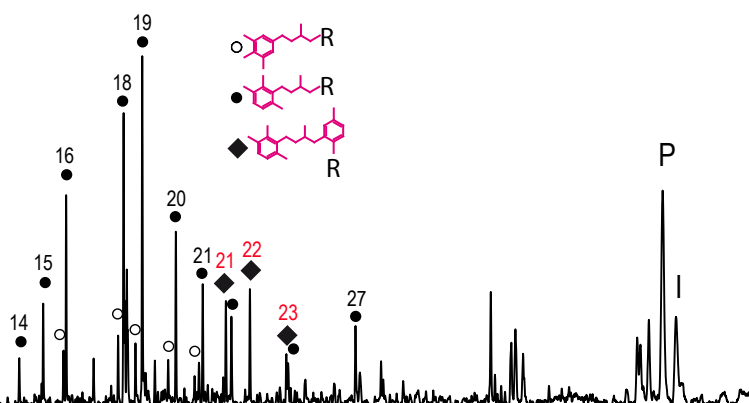
b) Bathurst TWC-28 Cape Philips Fm

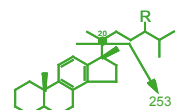


c) Southampton 07CYA-Z040-02 Red Head Rapids Fm



d) Heinrich Layer

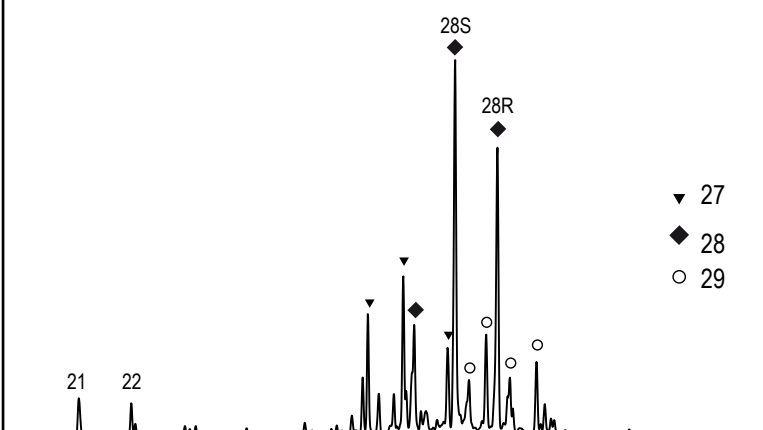




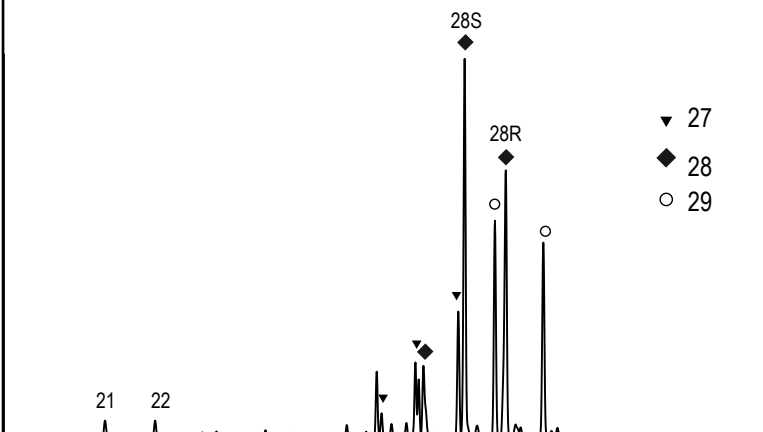
C-ring monoaromatic steroids

m/z 253

a) Baffin 11SZ-14-01 Forster Bay Fm



b) Southampton 07CYA-Z040-02 Red Head Rapids Fm



c) Heinrich Layer

